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THE INDUSTRIAL PROCESSING OF UNIDIRECTIONAL FIBER PREPREGS

B. Laird

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16. Abstract

A80-44924 # The industrial processing of unidirectional-fiber prepregs (Mise en oeuvre industrielle des préimprégnés à fibres unidirectionnelles). B. Laird (Ciba-Geigy France S.A., Rueil-Malmaison, Hauts-de-Seine, France). *Plastiques Renforcés, Fibres de Verre Textile*, vol. 19, July-Aug. 1980, p. 9-16. In French.

Progress made in the industrial processing of preimpregnated composites with unidirectional fibers is discussed, with particular emphasis on applications within the aerospace industry. Following a brief consideration of the aspect involved in the selection of industrial materials, attention is given to the conditions justifying the use of composites and the properties required of industrial prepregs. The hardening cycle is examined for the cases of nonmodified and polymer-modified resins, with attention given to the stabilization of flow, the necessary changes of state, viscosity control and the elimination of porosity. The tooling necessary for the fabrication of a laminated plate is illustrated, and the influence of fabrication and prepreg properties on the mechanical characteristics of a laminate are indicated. Finally, the types of prepregs available and the processing procedures necessary for them are summarized. A.I.W.

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THE INDUSTRIAL PROCESSING OF UNIDIRECTIONAL FIBER PREPREGS

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The industrial processing of unidirectional fiber prepregs can /9* be considered as the most complicated case. Woven fibers are in fact mechanically connected to each other, and their processing does not threaten to disturb their orientation.

We are therefore going to analyze the general features of the steps taken to perfect an industrial prepreg. But before entering into the heart of the matter, let us position ourselves a little bit upstream form fabrication and observe what occurs in research departments, which regularly have to decide which material to use based on the design of the component under development.

This choice is in particular guided by a certain number of considerations arising from the article's intended use. Among the most important of such considerations are thermal, mechanical, electrical, and chemical constraints, not to mention the applicable regulations. It should be noted that the subject of unidirectional fiber prepregs obviously concerns fibers with high mechanical characteristics. These are the ones which are most likely to interest research departments for use in load bearing structural components.

We will equally concentrate in this article on the aerospace industry. On the one hand, this is the field in which the most spectacular developments have occurred. On the the other, aerospace is one of the industrial sectors in which the use of composite materials is the most justifiable. Within this framework, let us /10 return to the criteria that research departments have to consider when choosing, and especially justifying the use of, composite materials.

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*Numbers in the margin indicate pagination in the foreign text.

Table 1
Constraints and Justifications

*Environmental Constraints

-- Rain
-- Air Friction
-- Solar Radiation and Ozone

*Operational Constraints

-- Mechanical
-- Thermal
-- Electrical
-- Chemical
-- Regulations

*Technical Justifications

-- Reduced Weight
-- Maintenance or Improvement of Mechanical Characteristics
-- Better Fatigue Resistance
-- Reliability Comparable to that of Metals

*Economic Justifications

-- Price of Products
-- Cost of Inspection upon Receipt
-- Cost of Storage
-- Cost of Processing, Including:
  Price of Tooling
  Consumption of Energy
  Scrapping of Products
  Reliability of Process
-- Cost of Quality Control

In table 1, which deals with constraints and justifications, we list:

-- environmental constraints,
-- operational constraints,
-- technical justifications, and
-- economic justifications.

If, therefore, all the parameters associated with the problems arising during the assembly of these materials are taken into consideration, it is explainable why the use of plastics and composite materials has not become more widespread in aeronautics. Remember

Table 2
Essential Characteristics Required of a Prepreg

1. Uniformity of module strength and of the ensemble of mechanical characteristics.
2. The closest possible tolerances in the areas of mass, size, and appearance.
3. No influence of fabrication techniques on the final properties of the composites.
4. Long shelf life.
5. Easy handling (drapability, interlaminar adherance).
6. Great range of fabrication techniques, including in autoclave, press, and filament winding machine.
7. Compatability with structural adhesives.
8. High thermal stability.
9. High resistance to aging.

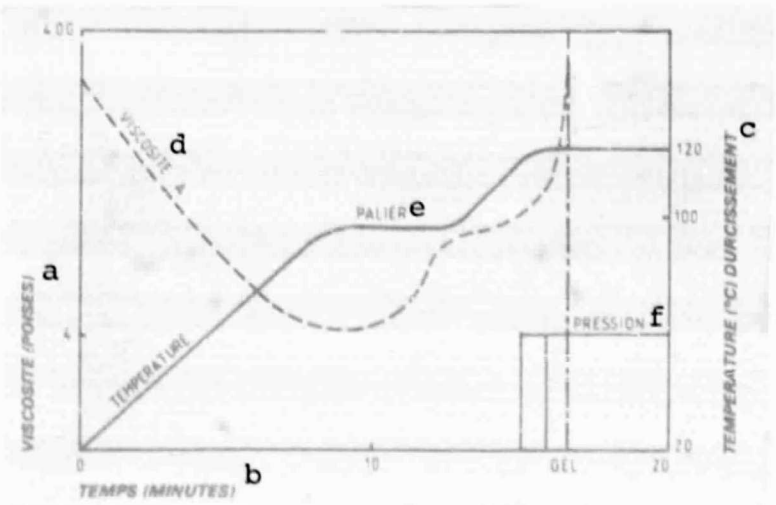

Figure 3
Matrix A -- Unmodified Resin

Key: a) Viscosity (Poises)
b) Time (Minutes)
c) Hardening Temperature (°C)
d) Viscosity A
e) Plateau
f) Pressure

that on the average, plastics make up only 5% of the mass of an airplane. The figure is only 2 to 3% for large transport aircraft, but attains 20% for certain types of light airplanes. Furthermore, most of the plastics used are for nonstructural applications. In a Boeing 727, for example, out of a total mass of 77 metric tons, a mere 3 tons of plastics are used, including close to one ton for the interior decor. The introduction of carbon fibers and their development over the last decade with the recognition of their superior qualities are an indication that plastics' role will increase in the future. In addition, their growth will take place not only in the fabrication of structural parts, but also in the design and construction of essential ones. The latter area in particular poses a serious problem for the user. It concerns the reliability of plastic materials. The guarantee of a high quality product resides in the ability of the prepreg maufacturer to reproduce such quality within a well-determined tolerance.

We have summerized the qualities which might be requested by the user of industrial prepregs in table 2. Points 1 and 2 in this table will depend mostly on the quality of the fibers and their distribution in the prepreg. The other points basically depend on the formulation of the matrix. The choice of matrix, which, the reader will recall, serves to bind the fibers together, therefore plays an essential role in fabrication and reliability. Fabrication will also strongly influence the economic aspect to the extent that the products impose a minimum of constraints on the design of tooling and on the the material's actual use. The most widely developed and employed formulations have been those with a modified epoxy base.

In figure 3, we have plotted the hardening cycle during industrial processing for a relatively simple system of formulation, hereinafter called matrix A.

One will immediately see in this diagram that as the temperature increases, the matrix's viscosity decreases. If, therefore, the pressure was applied in this cycle at a time T_0, the matrix would behave exactly like a fluid. Under the force of the pressure, /11

a large amount of resin would be pressed out from the fibers, and, in addition, their alignment in relation to each other might be greatly disturbed.

We therefore have to stablize the system's flow. This is the reason why we allow for a plateau. The higher degree of viscosity thus acheived allows the pressure to be applied at this stage without risk of disturbing the fibers' alignment. Hopefully, one can at this point press out the desired amount of resin while at the same time forcing out the air still remaining in the prepreg's various layers and thus obtaining a laminate of low porosity

In the cycle under consideration, we have not spoken of the conditions for positioning the prepreg and in particular of its drapability. The different layers should be placed on top of each other, and their sticking power, or adhesion, should be neither too high nor too low. The processor will often have to allow for a certain ripening of the matrix to achieve this level of adhesion.

This is the point of transition to stage B, which consists of triggering a reaction to bring the material to the desired state. Under such well-determined fabricating conditions, the proper adherence can be attained within a certain tolerance. However, once the reaction starts, it threatens to rapidly evolve, and the product's lifespan will then be shortened. The material's state changes as a function of its age and storage conditions, and it is necessary to adjust the plateau for each lot used. We have therefore decided that this system of formulation does not respond to the desire for simple, and therefore reproducible, industrial processing. All the experiments have clearly shown that the matrix's flow plays an essential role in the behaviour of the final laminate.

Dr. J. Johnson [1] arrived at identical conclusions and stressed the necessity of having a high degree of control over the viscosity of the matrix systems so that the lamination pressure is applied over as long a period as possible. This permits the elimination of porosity without having the problem of excessive resin flow, and thus drying

out the fibers too much. Having experimentally determined that the minimum viscosity for obtaining a controlled flow is 40 poises, research has been directed toward formulating matrices with the equivalent minimum viscosity at the hardening temperature.

Tests were then conducted in which the viscosity was adjusted by mixing solid and liquid resins. However, this resulted in relatively brittle matrices. Taking into account the various criteria and after numerous tests, the choice fell on fomulations with added thermoplastic polymer. Such an addition made it possible to stabilize viscosity over a wide temperature range and to produce less fragile matrices. The flow was thus controlled, and the strength of the impregnation system improved.

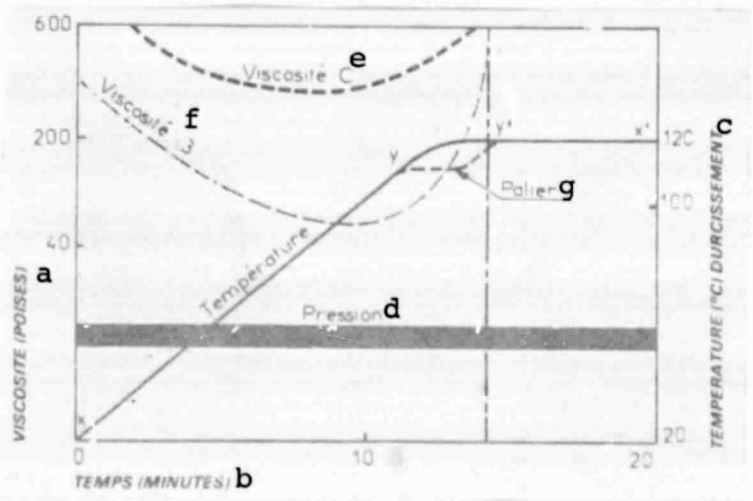

Figure 4
Polymer-Modified Matrix

Key: a) Viscosity (Poises)
b) Time (Minutes)
c) Hardening Temperature (°C)
d) Pressure
e) Viscosity C
f) Viscosity B
g) Plateau

It should be added that in this formulation, interlaminar adhesion is adjusted in the initial state by adding a mixture of resins at the necessary viscosity.

This is in stage A. The mixture's lifespan is therefore

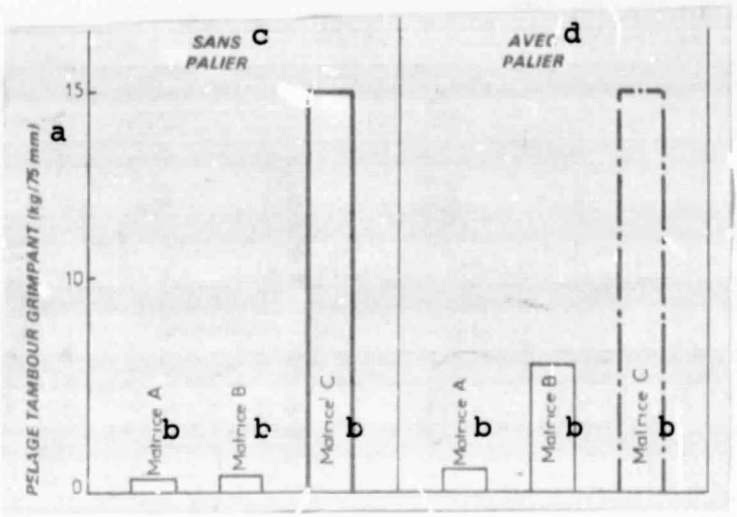

Figure 5
Peel Strength According to Matrix and Curing Cycle

Key: a) Climbing Drum Peel Strength
b) Matrix A, etc.
c) Without Plateau
d) With Plateau

unaffected, and it remains stable for a long time in storage.

The two formulations just mentioned are compared in figure 4. These are matrix B, whose viscosity is adjusted by mixing solid and liquid resins, and matrix C, whose formulation is modified by a polymer. Note that matrix B's minimum viscosity is above the previously mentioned 40 poise minimum.

This formulation allows the pressure to be applied during the entire hardening cycle (curve X-X'). The effectiveness of such control over viscosity is demonstrated by the values obtained, 1500 MN/m^2 at 22°C for flexural strength and 92 MN/m^2 for shear strength.

Meanwhile, if a laminated sheet is made directly on a honeycomb and if a peel test on a climbing drum is carried out, it is possible to compare the fragility of the systems on the basis of the measured peel strengths.

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Notice the high fragility of matrix B in figure 5. Once more, it is necessary to resort to a plateau (curve X-Y-Y'-X'). While the plateau very sharply increases peel strength by promoting meniscus formation on the honeycomb, the system produced is still very brittle. Matrix C's viscosity far exceeds the critical minimum, and the composites obtained have very acceptable values: flexural strength of 1350 MN/m^2 and shear strength of 82 MN/m^2, with good adherence in the case of <u>in situ</u> gluing on the honey comb (figure 5). /12

It has not been necessary to introduce a plateau for matrix C.

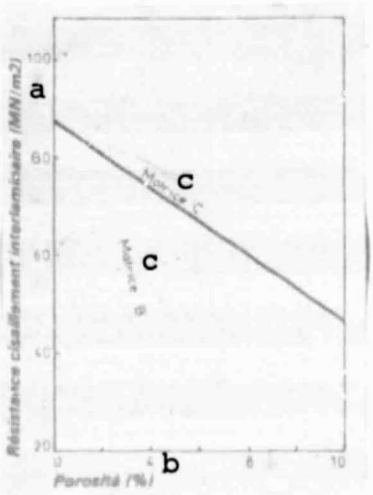

Figure 6
Effect of Porosity on Shear Strength

Vf = 0.60. High strength carbon fibers. Porosity measured by "Quantimet". Interlaminar measurements made according to NM 547.

Key: a) Shear Strength (MN/m^2)
b) Porosity (%)
c) Matrix

Finally, figure 6 shows the importance of eliminating porosity when using a type B matrix. It also shows how tolerant a type C matrix is.

When it is known that a proper fabrication procedure yields porosities of less than 0.5% with a certain matrix, simplified processing procedures can be introduced. Even if such processes result in greater porosity, the penalty in terms of shear strength is not great. It is in this way that Ciba-Geigy formulates its Fibredux prepregs and ensures that they have a long lifespan at ambient temperature, high mechanical performance, and, especially, high reproducibility with simplified processing procedures.

This group of qualities yields the reliability and the guarantee sought by the user.

There is one point that we have as yet mentioned only in passing. This concerns removing resin from the fibers. The prepregs generally offered have an excess of resin. When fabricating laminates, it is generally considered that optimal

properties are obtained when the volume of fibers reaches 60% of total volume. We will call this prameter Vf. It is the processing procedure which allows us to attain the ideal Vf. In addition, research departments determine the number of plies and their orientation in relation to the direction of 0° maximum stress as a function of the component under development and the magnitude and direction of stress.

Table 7
Nominal Fiber Weight for Various Hardened Ply Thicknesses (EP) at 60% Fiber by Volume (Vf) and for Various Types of Fibers

SYMBOL	EP. MM 60% VF	TS	MS	AS G/M2	K	R	E
4	0.1	106	112	108	87	155	152
4.5	0.115	121	129	124	100	178	175
5	0.125	132	140	135	109	194	190
6	0.150	158	168	162	130	232	228
8	0.200	211	224	216	174	310	304
10	0.250	264	280	270	218	387	380
DENSITY	G/CM3	1.76	1.87	1.80	1.45	2.58	2.54

$G/M2 = 0.6 \times \rho \times CPT \times 1000$

EP. Provisional BSD Standard
TS High Strength Carbon Fiber
MS High Modulus Carbon Fiber
AS Intermediate Carbon Fiber
K Kelvar (R) Fiber
R Glass R
E Glass E
(R) Registered Trademark

Table 7 gives a few examples of mass of fiber per ply for a few thicknesses as a function of the type of fiber used and its density. The formula gives the nominal thickness per hardened ply which should be attained in the laminate. /13

The excess resin in prepregs is necessary when gluing is carried out simultaneously with hardening on a honeycomb or porous material.

In contrast, it proves to be an annoyance when the industrial fabrication of composites is concerned.

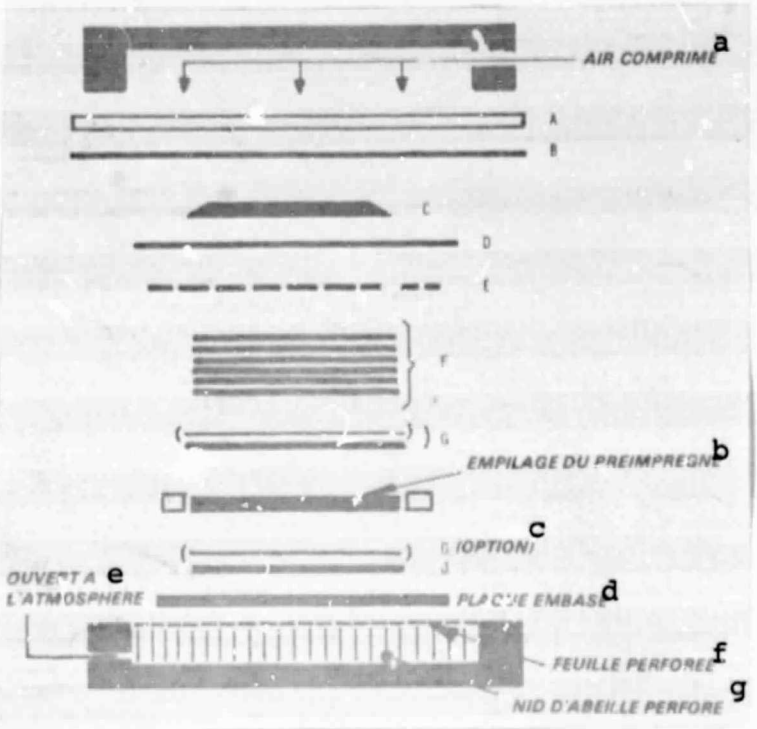

Figure 8
Tooling with Absorptive Fabric for the Fabrication of a Laminated Plate

A) Heat Resistant Elastomer
B) Nylon Pressure Bag (Dupont Capran 80)
C) 5 mm Thick Steel Plate
D) Drainage Material (Type 1581 Glass Cloth)
E) Sheet Similar to B, but Perforated in a Quincuncial Pattern by Small Pinholes
F) Stack of Absorptive Cloths
G) Set of Sheets to Delaminate
J) PTFE or Teflon Coated Glass Fabric or Other Unmolding Agent
K) High Temperature Resistant Elastomer or Synthetic Cork (e.g., Nebar from R. Klinger, Ltd.)

Key: a) Compressed Air
b) Prepreg Stack
c) (Option)
d) Base Plate
e) Open to Atmosphere
f) Perforated Sheet
g) Perforated Honeycomb

Figure 8 shows how complicated the laboratory tooling for fabricating a test plate is. Notice in particular the layers of absorptive fabric for soaking up the excess resin. The greater the

laminate's thickness and the more excess resin there is in the prepreg, the more absorptive layers are needed.

The excess resin is, however, considered necessary to ensure sticking power (among other things) and therefore the adherence between plies. Absorption of the excess therefore plays an important role in determining the composite's final properties, and, as we have seen, the controlled viscosity of the matrix aids us considerably in obtaining the ideal Vf.

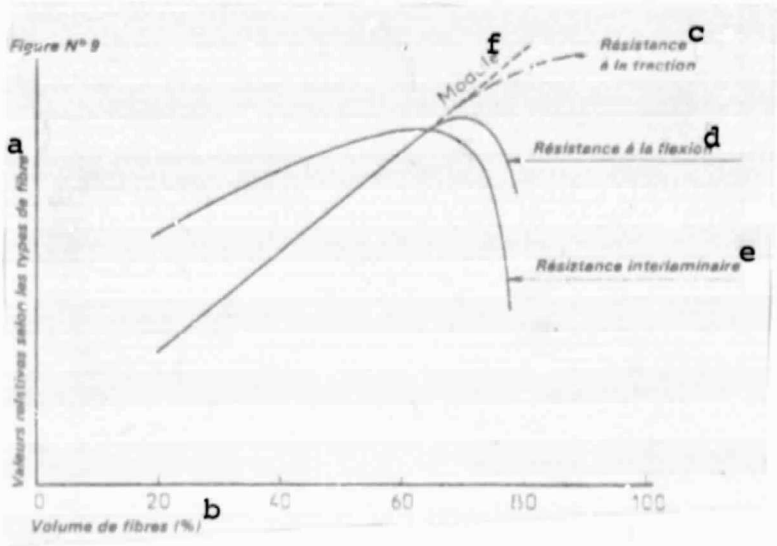

Figure 9
Influence of Fiber Content on Mechancial Properties

Key: a) Relative Values According to the Type of Fiber
b) Fiber Content by Volume (%)
c) Tensile Strength
d) Flexural Strength
e) Shear Strength
f) Modulus

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Figure 9 gives a general idea of the influence of processing techniques on a laminate's major characteristics. The fiber content has a particular influence on bending and stretching, while shear strength is less influenced by the fibers than by the porosity, as we have seen above.

In any case, absorption of excess resin is a constraint for

the user. It requires an extra operation during processing, thus incurring the risk of variation in the results and significant increase in costs. This is the reason why manufacturers more and more request prepregs whose fiber content is equal to that required in the hardened laminate.

To sum up, we show in the following tables the three types /14
of prepregs likely to be encountered, each one the result of a different type of processing.

Table 10 covers adhesive prepregs, i.e. those with a large amount of excess resin for adherence on a honeycomb or porous material. The excess resin could also be used for impregnating fabrics placed in interlaminar plies.

Table 11 deals with the prepregs used up to now, in which the amount of excess resin added depends on the type of fiber and its density.

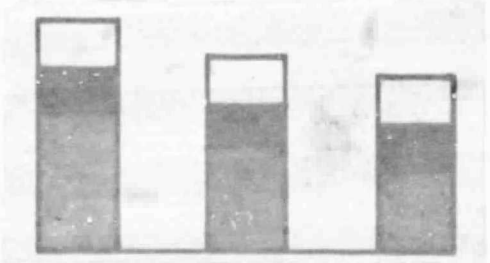
Lastly, table 12 concerns what could be called the new generation of prepregs. Such prepregs do not possess an excess of resin and make it possible to fabricate laminates with presses, autoclaves, and filament winding machines. In addition, given the characterisitics of controlled flow Fibredux matrices, low porosity laminates with an optimal fiber content can hopefully be fabricated under simplified /15
conditions. Numerous tests and fabrications have been carried out with the the new prepregs, and all the results encourage us to pursue this line of research. It can be added that the sticking power, which was the unkown factor, is sufficient to ensure the adherence of the different plies.

In conclusion, it can be hoped that this is a step in the direction of the greater reproducibility requested by users. This type of matrix simplifies the task of manufacturers and thus contributes to the economic side of the question. /16

Improvements in weight, reliability, and economics are important

factors favoring the choice and therefore the development of composite materials.

Table 10
Justifications, Advantages, and Drawbacks
of Fiber and Resin Levels in Unidirectional Prepregs

1. Resin Content	HIGH		
2. Type of Fiber Reenforcement	GLASS	CARBON	KEVLAR
3. Typical Fiber Density in g/cm^3	2.58	1.76	1.45
4. Ideal Fiber Content by Volume Generally Considered Optimal for a Laminate	0.60	0.60	0.60
5. Reason for Particular Resin Content	In situ hardening of thin composite sheathing (0.1 to 1 mm) on honeycomb or powdered material for sandwhich structure. Excess resin can be used to impregnate dry woven fabrics in interlaminar plies in the component.		
6. Typical Prepreg Resin Content by Weight (%)	40	50	55
7. Excess Resin in Prepreg over that Required to Attain Ideal Vf Expressed as % of Total Resin Weight	57	57	57
8. Excess Resin in Prepreg over that Required to Attain Ideal Vf, Expressed as % of Total Prepreg Weight	23	28	31
9. Graph of Composition by Weight			
10. Ease of Obtaining Ideal Vf	Resin must be of high viscosity to stick well on honeycomb. However, process is more complicated for attaining ideal Vf.		

Excess Resin

Resin Necessary for Ideal Vf

Fiber

11. Drawbacks of this Resin Content	a) High viscosity systems: Vf cannot be reached without special techniques for absorbing excess resin. b) Low viscosity systems: Impossible to get good adherence to the core. Absorption of excess resin facilitated by external absorption or drainage into reservoirs of sufficient size.
12. Comments	Adherence to core can be improved by incorporation of thixotropic agents.

Table 11
Justifications, Advantages, and Drawbacks
of Fiber and Resin Levels in Unidirectional Prepregs

1. Resin Content	MEDIUM		
2. Type of Fiber Reenforcement	GLASS	CARBON	KEVLAR
3. Typical Fiber Density in g/cm^3	2.58	1.76	1.45
4. Ideal Fiber Content by Volume Generally Considered Optimal for a Laminate	0.60	0.60	0.60
5. Reason for Particular Resin Content	a) Resins of medium and low viscosity: Standard prepregs for the fabrication of monolithic laminated components. b) High viscosity resins: Possible to harden thin sheaths (0.1 to 1 mm) in one operation on nonporous substrates.		
6. Typical Prepreg Resin Content by Weight (%)	34	42	48
7. Excess Resin in Prepreg over that Required to Attain Ideal Vf, Expressed as % of Total Resin Weight	43	43	43
8. Excess Resin in Prepreg over that Required to Attain Ideal Vf, Expressed as % of Total Prepreg Weight	15	19	21

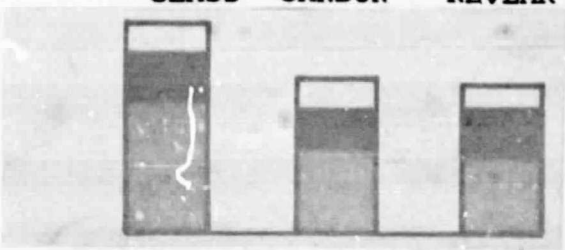
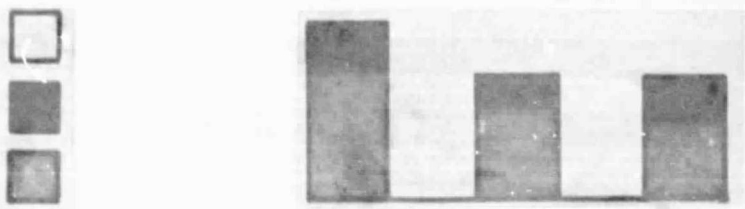
9. Graph of Composition by Weight	Excess Resin Resin Necessary for Ideal Vf Fiber	
10. Ease of Obtaining Ideal Vf		a) Low viscosity resins: Components of medium thickness without problem; thick laminates require higher pressures. b) Medium viscosity resins: Higher pressures required to drive out the excess resin. c) High viscosity resins: Same as for prepregs with a high resin content.
11. Drawbacks of this Resin Content		a) Low viscosity resins: High flow means that high absorption control (according to resin's state of development) required to obtain good lamination. b) Medium viscosity resins: More sophisiticated methods such as preconsolidation required for thick sections (5 to 50 mm). c) High viscosity resins: Same as for high resin content prepregs.

Table 12
Justifications, Advantages, and Drawbacks
of Fiber and Resin Levels in Unidirectional Prepregs

1. Resin Content	LOW		
2. Type of Fiber Reenforcement	GLASS	CARBON	KEVLAR
3. Typical Fiber Density in g/cm^3	2.58	1.76	1.45
4. Ideal Fiber Content by Volume Generally Considered Optimal for a Laminate	0.60	0.60	0.60
5. Reason for Particular Resin Content	Fabrication of thick or thin monolithic laminates without absorption reservoirs or drainage systems in the mold.		

	GLASS	CARBON	KEVLAR
6. Typical Prepreg Resin Content by Weight (%)	24	32	36
7. Excess Resin in Prepreg over that Required to Attain Ideal Vf, Expressed as % of Total Resin Weight	0	0	0
8. Excess Resin in Prepreg over that Required to Attain Ideal Vf, Expressed as % of Total Prepreg Weight	0	0	0

9. Graph of Composition by Weight



10. Ease of Obtaining Ideal Vf — No problem with eliminating porosity.

11. Drawbacks to this Resin Content — Impossible to use single operation gluing processes without excess resin; prepreg's visual appearance might appear affected because missing resin does not mask possible gaps between strands.

REFERENCE

[1] Johnson, J. "Resin Matrices and their Contribution to Composite Properties", New Fibers and their Composites, Transactions of the Royal Society, London, 1978.